Evaluation of Novel Autonomous Self-Healing Polymer Composite

by

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Submitted to the Department of Materials Science and Engineering
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Abstract

Autonomous self-healing materials offer a novel ability to self-repair damage caused by fatigue or fracture. Applications in many industries, from medical to aerospace, suffer from formation of microcracks, which often result in catastrophic failure of the product when the cracks remain undetected. A self-healing material capable of microcrack elimination would improve the safety of such products, as well as extend their lifetime.

This paper presents several recently developed autonomous self-healing designs of polymer composites. The commercialization potential of the designs is explored. Potential applications in four industries are identified, and the helicopter blade is selected as the most likely application to succeed in introducing the novel material into the market. The helicopter market is evaluated based on demand, growth, stability, and ease of entry. Intellectual property landscape is presented and competitors are identified. A combination business strategy of research and development and intellectual property licensing is recommended for entry into the helicopter market.

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1. Background

1.1 Historical Perspective

For centuries, the design of engineering materials with desired properties has been based on the concept of damage prevention. In other words, it has been recognized that continuously increasing level of damage due to exposure of the material to critical loads would lead to formation of cracks within the structure, which would be difficult to detect and repair, thus inevitably resulting in failure. The only apparent solution was to design a material with properties that would enable it to delay the onset of damage and to decrease the rate of damage formation. To accomplish this, the accepted strategy was to control and fine-tune the material production process. A successful process would enable placement and immobilization of atoms of the material into the “correct” positions, while avoiding production defects. The new material, improved via a superior production process, would potentially be able to sustain larger loads for longer periods of time without forming micro-cracks, thus slowing down the effects of damage. However, in the lifetime of the material, the damage level as a function of time is either constant or increasing. Thus, a reduction or removal of a load that caused damage would not decrease the level of damage. Eventually, the material would reach a critical level of damage, and fail catastrophically. [1]

Recent development of self-healing materials has introduced an alternative method for engineering materials design: the concept of damage management. This novel concept acknowledges the high probability of damage occurrence, but it regards damage formation as unproblematic as long as it can be counteracted by an autonomous process of healing. The ability to effectively remove damage would enable the material to undergo periods of negative rates of damage formation, thus expanding the lifetime of the product manufactured from such autonomously self-healing materials. The net performance of the material would depend on the rate of damage formation and the rate of damage healing. [1]

The design of a self-healing material needs to take into consideration the following characteristics. Because it is meant to substitute the currently used structural material, the self-healing material has to be able to perform regular mechanical functions that are required by the application of interest. Initially, a fraction of the material has to be mobile in order to be able to travel to and fill the local damage spots. However, once in place, the healing material has to bond the surfaces of the damage site and remain immobile for the remaining lifetime of the product. A damage sensor or a healing trigger has to be incorporated into the material in order to initiate the healing process. Ideally, the damage itself would be such trigger. In order for healing to occur, the surfaces of the damage site have to remain in close proximity to each other. Self-healing materials are more likely to succeed under cyclic rather than constant loads. When a load is temporarily removed, the probability of further crack propagation is reduced.

Design of self-healing materials is currently in early stages of development. It is likely that various desired properties of such materials would be addressed and incorporated in stages, rather than all at once. It is therefore useful to identify the minimal properties a material needs to possess in order to be considered self-healing. The end goal, however, is to produce an ideal self-healing material. The minimal and ideal properties of self-healing materials are defined in Table 1 below.

Table 1. Properties of ideal and minimal self-healing materials [1]

Ideal Self-Healing Material	**Minimal Self-Healing Material**
Can heal damage many times	Can heal damage only once
Can heal damage completely	Can heal damage partially
Can heal defects of any size	Can heal small defects only
Performs healing autonomously	Requires external assistance to heal
Equal/superior properties to current materials	Inferior properties to current materials
Cheaper than current materials	Extremely expensive

Self-healing materials began to attract some attention in the 1970's, when it became necessary to understand the properties of filled elastomers, such as the ones used in solid rocket propellants in space exploration. It was discovered that formation of cracks in such elastomers could be reversed via self-healing by removing the load and allowing some time for the healing process. In the late 1980's and early 1990's, further research lead to the discovery of self-healing ability of the thermoelastic polymers. Cracks in materials such as poly(methyl methacrylate) could be completely removed by heating the material to temperatures above T_g (glass transition temperature). [2]

The issue that needed to be addressed next was imparting of the self-healing property onto thermosetting materials, which are rigid below T_g, such as the ones used in composite matrices. In 1993, Carolyn Dry (University of Illinois at Urbana-Champagne) developed a passive self-repair polymer/fiber composite system [3]. The material consisted of an epoxy polymer matrix, structural metal fibers, and two types of hollow fibers. One type of hollow fiber was filled with an epoxy monomer, while the other type contained a diamine cross-linking agent (see Fig. 1). In this setup, the type of damage that the composite material was meant to heal was debonding of the metal fibers from the epoxy matrix. To test the self-healing ability, the metal fibers were first manually mechanically debonded from the matrix. Then, the composite was subjected to loads which were sufficient to crack the walls of the hollow fibers carrying the healing reagents. The epoxy monomer and the cross-linking agent fluids migrated to the polymer-metal interface via diffusion, where they reacted to repair the damage. After curing, attempts to pull out the metal fibers indicated that the system had successfully healed the debonding damage, and considerably increased the fiber pullout stress.

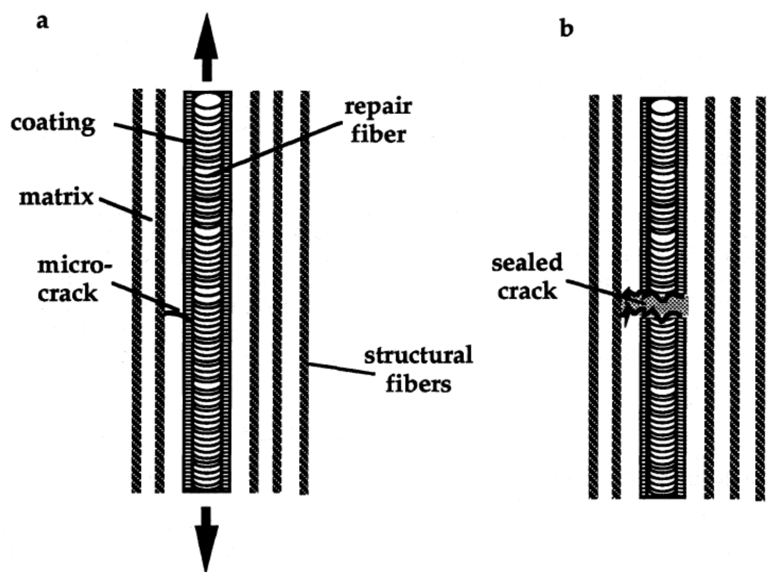

Fig. 1 Passive self-repair polymer/fiber composite system [3]

In 2001, Scott White and Nancy Sottos (University of Illinois at Urbana-Champagne) developed a different passive self-healing composite system [4]. They argued that hollow fibers are likely to provide the undesirable areas of high stress concentration. Instead, they encapsulated the cross-linking healing reagent in microcapsules. These microcapsules, as well as catalyst particles necessary to initiate the healing reaction, were embedded in an epoxy polymer matrix. A propagating crack formed within the material would rupture the microcapsules, thus releasing the healing reagent into the crack, and healing the damage. As such, the system was able to remove the microcrack damage by self-healing autonomously, without manual intervention. The microencapsulation design is described in detail in the “Designs of Self-Healing Materials” chapter.

1.2 Technical Background

The type of damage that the autonomously self-healing design developed by White and Sottos is meant to heal is microcracks formed on the surface or within the material. In order to examine the self-healing ability, the material undergoes the following procedure. First, the sample is fractured or fatigued until a single crack is formed. Various fracture properties, such as the stress intensity factor (K_{IC}), fracture energy (G_{IC}), or crack growth rate (da/dN) (where a is the crack length and N is the number of fatigue/load cycles) are measured. After the crack is formed and propagated, the surfaces of the damage site are brought back in contact with each other. The material is allowed to heal at a specified temperature for a specified period of time before it is refractured in the same manner as described above. The fracture properties of the virgin material and the healed material are compared.

The exact mechanism of crack healing in epoxy has not yet been fully understood. It is likely that fracture creates many new polymer chain ends at the surfaces of the damage site, and these chain ends become available for interdiffusion at the interface. Also, it is possible that when the damage site surfaces are brought together, they provide new spatial orientations and arrangements of the functional groups, thus leading to additional curing. [5]

In order to measure the efficiency of self-healing, the fracture toughness (K_{IC}) values of the healed and the virgin samples are compared. In the experimental setup for testing the designs described in the “Designs of Self-Healing Materials” chapter, the samples have a tapered double-cantilever beam (TDCB) geometry [6]. The corresponding formula for fracture toughness of a TDCB sample is

$$K_{IC} = 2 P_C \frac{\sqrt{m}}{b} \tag{1}$$

where P_C is the critical fracture load, and m and β are geometric parameters. The healing efficiency is defined as

$$h = \frac{K_{IC\,healed}}{K_{IC\,virgin}} \tag{2}$$

However, for a given sample, the geometric considerations remain unchanged. Therefore, the healing efficiency can be simplified to be the ratio of the critical fracture loads:

$$h = \frac{P_{C\,healed}}{P_{C\,virgin}} \tag{3}$$

2. Designs of Self-Healing Materials

Design of the autonomous self-healing material of interest is based on incorporation of a catalyst and a healing reagent within an epoxy matrix. Two designs with self-healing capability are described below.

2.1 Design #1: Microencapsulation

The microencapsulation design includes a dispersion of solid catalyst particles, as well as microcapsules containing a healing reagent, within an epoxy matrix. In this particular design, the matrix consists of EPON 828 epoxy with a diethylene triamine curing agent; the catalyst dispersed throughout the matrix is Grubbs catalyst (see Appendix for details); and the healing reagent enclosed in the poly(urea formaldehyde) microcapsules is dicyclopentadiene (DCPD). The size of the catalyst particles varies from 180 to 350 μm in diameter. The diameter of microcapsules varies from 180 to 460 μm, while the wall thickness ranges from 160 to 220 nm. [6]

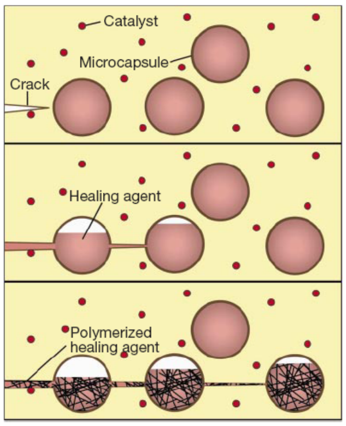

Fig. 2 Microencapsulation design. [4]

The healing mechanism is demonstrated in Fig. 2. As a crack forms on the surface or within the matrix at the site of the damage, it propagates into the bulk of the material. Upon encountering the microcapsules filled with the healing reagent, the crack ruptures the microcapsules, thus releasing the healing reagent into the crack plane via capillary action. Inside the crack plane, the healing reagent comes into contact with the catalyst particles, and a cross-linking polymerization reaction is triggered. After the healing process is complete, the surfaces of the crack are bonded together.

While the microencapsulation design can be utilized for various combinations of component materials, the materials in this particular version are chosen for the following reasons. In order for the crack to propagate through the microcapsule, and not around it, the microcapsule shell needs to be more compliant than the matrix. Selecting poly(urea formaldehyde) for production of the microcapsule shell satisfies this requirement. The healing reaction occurs by cross-linking dicyclopentadiene via living ring-opening metathesis polymerization (ROMP). The ROMP-based system is chosen for the self-healing design due to its long shelf life, low monomer viscosity and volatility, relatively rapid polymerization at room temperature, and low shrinkage upon the completion of polymerization. The unterminated chain ends involved in a living polymerization allow for multiple healing events. Grubbs catalyst is the appropriate choice for this particular system. [4]

Tapered double-cantilever beam (TDCB) samples of self-healing composites are manufactured and tested (see Fig. 3). Such TDCB geometry allows for controlled crack growth along the center of the sample. As described in the “Technical Background” section, the fracture toughness of such sample is independent of the crack length, and is easy to quantify using only critical fracture loads values. In order to propagate a crack in the sample, the material is loaded in tension, perpendicular to the crack plane.

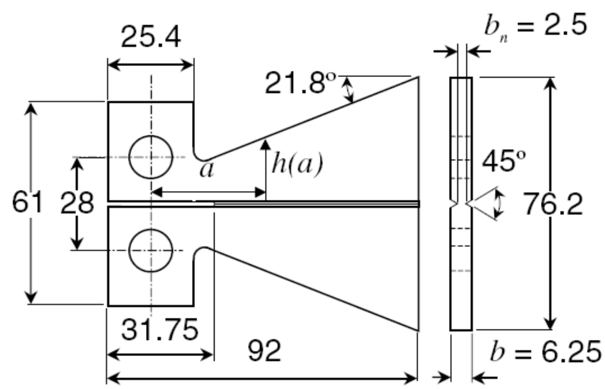

Fig. 3 Tapered double-cantilever beam (TDCB) geometry. Dimensions are in millimeters. [6]

Results of optimization of the self-healing process suggest that this design performs best at 2.5 wt% catalyst concentration and 5 wt% microcapsule concentration. In order to quantify the self-healing ability, the healing efficiency is measured (see equation 3). Experimental results indicate that if the material is allowed to self-heal at room temperature for 10 hours after crack propagation, average healing efficiencies of 85±5% can be achieved. [6]

Besides enabling the material to achieve high levels of self-healing, the microencapsulation design provides an additional benefit of improved fracture toughness in the virgin material due to inclusion of microcapsules and catalyst particles within the epoxy. The distribution of capsules and particles in the matrix of the material limits crack growth and propagation via crack pinning mechanism. “Tails” characteristic of the crack pinning toughening mechanism are shown in Fig. 4. The average critical facture load value for virgin samples with microcapsules and catalyst particles was found to be 20% larger than the average value for a neat epoxy material.

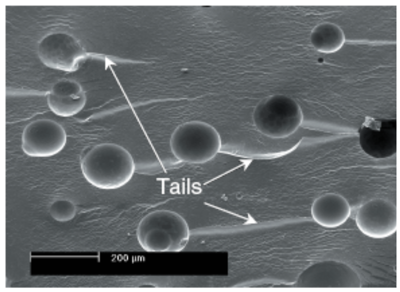

Fig. 4 Crack pinning mechanism. [6]

There are a couple of drawbacks to the microencapsulation design. At any given damage spot, the self-healing process can occur only once because after a crack is healed, the healing reagents in that region are depleted. Another drawback of this design, which could become a critical issue in the event that such a material is applied commercially, is the high cost of the Grubbs catalyst.

2.2 Design #2: Microvascular Network

The microvascular network design is inspired by the human skin. It is similar to the microencapsulation design in that it utilizes the same materials for the matrix, catalyst, and healing reagent. While the Grubbs catalyst is still dispersed throughout the epoxy matrix, the DCPD cross-linking reagent is no longer encapsulated in spheres. Instead, it is contained within a three-dimensional network of microchannels (Fig. 5). This 3D scaffold of microchannels, which are 200 μm in diameter each, is manufactured via robotic direct-write assembly. The vertical channels are designed to deliver the DCPD healing reagent to the cracks in the epoxy matrix. The entire microchannel network can be filled from the side of the sample via the horizontal channels. The channels are made from EnviroTex Lite epoxy, which is a less brittle material than the epoxy used for the matrix. Therefore, the surface of the microchannels does not create an area of high stress concentration. Instead, when a crack forms on the surface or within the material, it propagates toward the more compliant regions, which are located at the interface of the epoxy matrix and the microchannels (Fig. 6). The crack ruptures the surface of the microchannel, allowing the low viscosity healing reagent to flow into the crack plane. Upon contact with the DCPD monomer in the crack site, the solid phase catalyst particles quickly dissolve and react [7]. The details of the healing process remain the same as in the microencapsulation design.

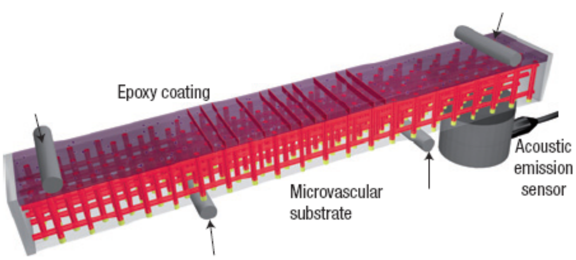

Fig. 5 Microvascular Network design. [7]

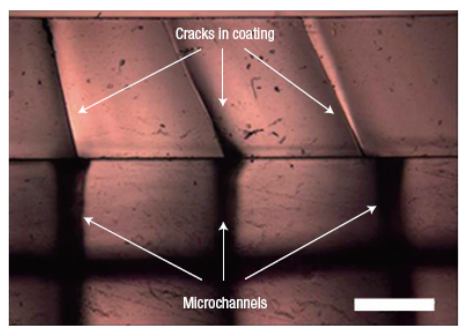

Fig. 6 Crack propagation. [7]

To determine the healing efficiency of the microvascular network design, the sample is loaded in four-point bending, as indicated by the arrows in Fig. 5, until a single crack is formed on the surface. Then, the load is removed, and the material is allowed to heal. At 10 wt% catalyst concentration, if the material heals at room temperature for 12 hours, healing efficiencies of up to 70% could be achieved. While enabling the material to achieve reasonable levels of self-healing, this design offers an important advantage over the microencapsulation design. The system of microvascular channels allows self-healing to occur successfully on the same damage spot up to seven times.

There are several drawbacks to the microvascular network design. As mentioned earlier, the Grubbs catalyst is very expensive relative to the rest of the components of this material, and this design uses catalyst concentrations that are four times higher than the microencapsulation design. This design is also more expensive due to the use of robotic assembly in the network manufacturing process. Lastly, while the microchannels allow the material to heal multiple times in the same damage spot, eventually the healing reagents are depleted. The issue of re-supply of the healing reagents needs to be addressed in order to make this material truly autonomously self-healing.

2.3 Ongoing Research

The current ongoing research is aimed at improving the designs described above. One focus of such research is replacement of the expensive Grubbs catalyst with significantly more affordable organic solvents [8]. The study is based on the microencapsulation design with the following modifications. The Grubbs catalyst particles are no longer dispersed within the epoxy. Instead, an organic solvent is encased within the same type of poly(urea formaldehyde) capsules as those used for containment of DCPD in the microencapsulation design. The healing mechanism in this case involves swelling of the bulk material using the solvent, which results in reptation and interlocking of polymer chains across the crack plane. Using 20 wt% chlorobenzene-filled microcapsules, and healing at room temperature for 24 hours, average healing efficiencies of 82% have been achieved. Higher efficiencies are possible if other, more polar solvents (such as nitrobenzene, *N*-methyl pyrrolidone, dimethylacetamide, dimethylformamide, and dimethyl sulfoxide) are used. However, these types of solvents have not yet been successfully encapsulated into a poly(urea formaldehyde) shell.

Another area of research involves incorporation of carbon fiber reinforcement into the epoxy matrix of the self-healing material, using the microencapsulation design [9]. The goal is to extend the self-healing ability to structural applications that require the material to carry greater loads. Carbon fiber reinforcement is introduced in the form of a plain weave fabric. Self-repair of delamination damage in width-tapered double cantilever beam (WTDCB) samples is investigated. At 5 wt% Grubbs catalyst and 20 wt% DCPD-filled microcapsules, after the material is allowed to heal at room temperature for 48 hours, average healing efficiencies of 38%, and maximum 45%, can be achieved. At an increased temperature of 80°C, the healing efficiency reaches up to 80%. This indicates that insufficient degree of cure occurs at room temperature. Another problem with this design is lowered virgin interlaminar toughness, most likely due to increase in interlaminar thickness caused by size and concentration of microcapsules and catalyst agglomeration. Further research efforts are going on to address these issues.

3. Potential Applications

If an epoxy polymer can be designed to function as a truly autonomous self-healing material, the possible applications of such a polymer are endless. However, taking into account the limitations of the current self-healing design, as well as recognizing the need to identify an application and market to enter in the short-term, this analysis will focus on specific applications within four major industries.

3.1 Microelectronics Packaging

An application within the microelectronics industry that could benefit from a self-healing capability is microelectronics packaging. Microelectronics packaging is a complex structure with numerous components. Fig. 7 demonstrates a typical layout of a flip-chip. This “face-down” flip-chip configuration offers numerous advantages over the traditional “face-up” wire bonding technologies, such as higher packing density, shorter interconnection length, better electrical performance and better manufacturability [10]. However, one of the major challenges that this technology had to overcome was the effect of the mismatch of the coefficients of thermal expansion (CTE) between the silicon chip and the substrate on solder joint reliability. The solution to the problem was to introduce an underfill layer between the silicon chip and the substrate. This layer consists of particle-filled epoxy layer with low CTE, which closely matches the CTE of the solder.

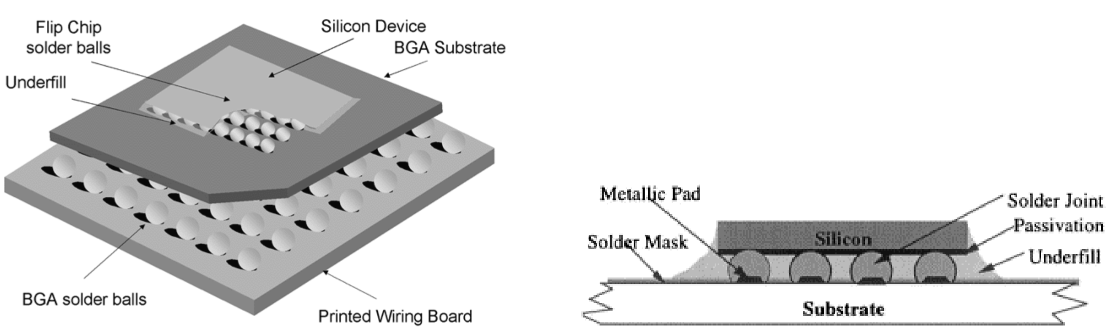

Fig. 7 Layout of a flip-chip. [11, 10]

Introduction of the underfill layer has greatly improved the life time of the microelectronics technology. Over the last two decades, a great amount of research has been aimed at improving the thermal and rheological properties of the underfill materials, in order to improve the underfill layer manufacturing process. One important issue that has been addressed is the void level in the underfill layer – voids between solder balls can result in electrical shorts. However, there are two other major issues with the underfill layer that have yet to be successfully resolved. Firstly, interfacial delamination between the underfill layer and the substrate or the silicon chip may result in solder ball fracture, which could lead to open electrical circuits. Secondly, cracks that form in the underfill material due to fatigue can propagate through the substrate, cutting the copper traces and once again resulting in open electrical circuits. Underfill fatigue cracking is one of the leading failure modes in microelectronics packaging technology. Introduction a self-healing polymer composite underfill layer at the substrate-silicon chip interface could potentially reduce delamination, as well as eliminate fatigue cracks, thus effectively extending the life time of the microelectronics technology.

While a self-healing capability is desirable for microelectronics packaging, there are several issues that could prevent the self-healing design discussed in the "Designs of Self-Healing Materials" chapter from being used in this application. So far, the self-healing concept has been shown to work on materials of approximately 10-20 mm thickness. It is yet to be proven that the self-healing property can be successfully imparted upon an epoxy material on the small scales within which the microelectronics industry operates (the underfill layer is typically 25 to 75 μm thick). Recent research results [12] demonstrate an ability to reduce the microcapsule size from approximately 200 μm to as small as 200 nm in diameter. This capsule size reduction leads to improved fracture toughness over the current microencapsulation design. However, self-healing efficiencies of epoxies with nanocapsules have yet to be determined.

Another issue that needs to be explored prior to introducing this self-healing design into microelectronics packaging is the effect of exposure of the composite material to high temperatures, which these kinds of applications face on a regular basis. Yet another issue concerns the manufacturing process of microelectronics packaging. Currently, there are several methods for incorporating the underfill layer into the packaging. A method that would be appropriate for incorporating the self-healing polymer composite involves pre-application of the underfill material before the solder balls are added. However, such process is highly susceptible to contamination of the solder balls, which could result in high resistance, poor electrical connection, and short product life. The preferred method is filling in the gap between the silicon chip and the substrate after the solder balls are already in place. To accomplish this, the epoxy has to be in a liquid state. The manufacturing challenge of incorporating the self-healing polymer composite into the current methodology is compounded by the multi-step process necessary to create the polymer composite, which is solid in its final form.

3.2 Automotive Coating

The automotive industry is constantly searching for ways to improve on their products. A particular component for which self-healing ability is desired is the automotive coating.

The coating consists of several layers (see Fig. 8). The body is the surface of the automobile, and is usually made of metal or a composite, such as plastic or fiberglass. The E-coat is the first paint layer, which protects metal car components from corrosion. The function of the primer is to create an optically uniform base for the color coat. The color coat, which is usually 25 to 50 μm thick, defines the primary color of the automobile, but offers no chemical or physical protection. The clear coat, which is the thickest of all the paint layers at 50 to 100 μm, is essentially responsible for all the chemical and physical protection of the car surface and the layers below. This clear coat, or top coat, is usually polyurethane-based. A clear coat that would be able to heal itself in the event of a scratch on the surface of the car is of great interest to the automotive industry.

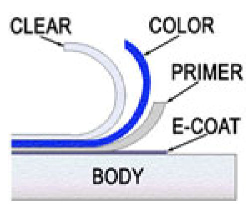

Fig. 8 Coating layers of car paint. [13]

There are several issues that could prevent incorporation of the self-healing design at hand into an automotive coating layer. The current thickness of the design is too large for automotive coating application. However, even if the dimension issue could be overcome, a more significant problem is that a self-healing material targeted for automotive coating has already been developed. Bayer Materials Science Coatings has developed a plasticized, highly cross-linked polyurethane based clear coat, which is able to self-heal with up to 90% efficiency [14]. The heat necessary to promote the healing process can be provided by the sun in sufficient amounts, and the reaction is completed within minutes. Moreover, polyurethane is significantly cheaper than the designs discussed earlier in this report, and this technology is already market ready. It would be very difficult, if not impossible, to compete with this technology based on cost and timeline to commercialization.

3.3 Hip Joint Replacement

Hip joint replacement is one of the applications in the medical industry that could benefit from a self-healing material. Currently, if a part of the hip joint replacement becomes damaged to the point of failure, there is no method to repair or replace the part without subjecting the patient to another surgery.

The materials currently used in hip joint replacement parts (see Fig. 9) include chrome, cobalt, titanium, and ceramic. There is one component, the insert between the acetabular cup and the femoral head, which is often made from a plastic material, namely ultra high molecular weight polyethylene (UHMWPE). This material has been successfully used in hip replacements for over 40 years, and the highly cross-linked version has been utilized since 1998. There are at least five years of clinical data available for UHMWPE. It is also relatively cheap, compared to the self-healing designs described in the “Designs of Self-Healing Materials” chapter.

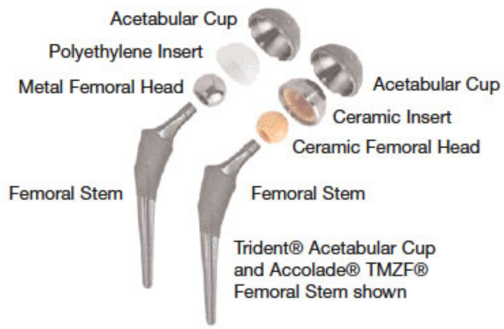

Fig. 9 Hip joint replacement prosthesis. [15]

It seems unlikely that the current self-healing design could compete with UHMWPE based on cost. Moreover, there are other barriers of entry that would prevent the use of such design in a hip joint replacement application. The novel material would need to obtain FDA approval, which involves a long and expensive process, complete with clinical trials. More importantly, the current design does not provide a structural material that would be able to carry the loads required by the hip joint replacement application.

3.4 Helicopter Rotor Blade

One of the many applications within the aircraft industry that could benefit from a self-healing capability is the helicopter rotor blade. As Fig. 10 indicates, the helicopter rotor blade is a complex structure with numerous components. One important component of the blade is the skin, which consists of multiple fiberglass layers. As with any technology, the probability of failure goes up with increased complexity of the structure. One mode of failure that occurs within the rotor blade is delamination of the fiberglass skin layers, either from each other or from the metal surface (see Fig. 11).

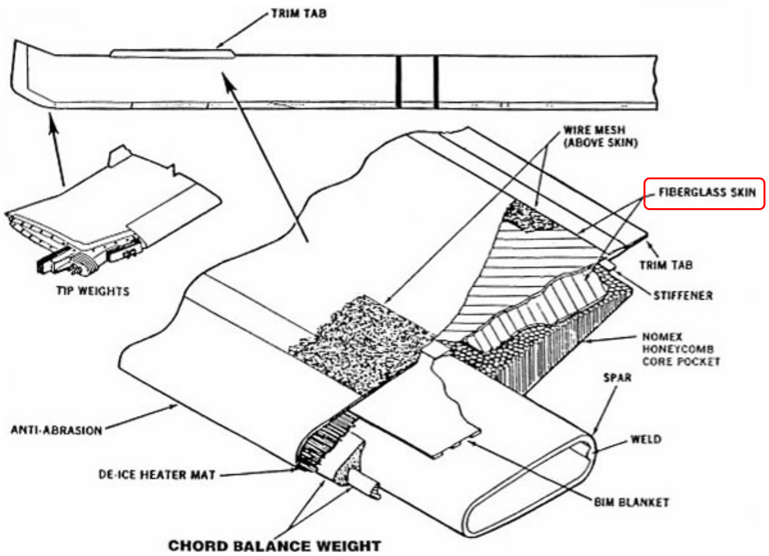

Fig. 10 Cross-section of the helicopter rotor blade. [16]

Fig. 11 Delamination in the helicopter rotor blade. [17]

Current methods of dealing with delamination include using extensive manual inspection techniques to determine the extent of the damage. For critical parts, such as the rotor blade, non-destructive testing techniques are utilized during the inspection. These techniques include ultrasonics, infrared thermography, X-ray tomography, and computerized vibro thermography [9]. These procedures are expensive and time consuming, and they require highly skilled labor. A popular non-destructive technique used specifically to detect cracks in rotor blades is eddy-current testing [18]. Electrical current is passed over the surface of the blade in order to locate cracks as small as one eighth of an inch in depth. The cost of this procedure is approximately $10,000 to $15,000 per unit.

If the delamination damage is found to be too severe, the structural component is replaced entirely. In case of less extensive damage, repairs are attempted. Localized delamination can be repaired either by injecting resin via an access hole into the failed area, or by bonding or bolting a reinforcing patch to the composite structure. The repair methods are costly and very labor-intensive, and require manual intervention by trained technicians. The cost of repair of the part (not including the inspection cost) increases exponentially with each inspection, up to 50% of the part replacement cost. If the cost of the repair is estimated to be larger than 50% of the replacement cost, the part is replaced entirely [19].

The lifetime of a rotor blade on an active military rotorcraft varies from 20 to 200 flight hours. For instance, Robinson helicopters used in the Gulf war were experiencing delamination due to moisture seeping in between the fiber layers, causing the extremely short rotor blade lifetime of 20 hours. To resolve this issue, rotor blades were covered in an epoxy tape, which was developed by Airwolf Aerospace specifically for Robinson helicopters. The lifetime of the blade increased to 200 hours [18].

The epoxy tape solution was developed specifically for only two models of helicopters. While it prevents delamination by applying external pressure onto the blade, it does not address the essential issue of layer debonding. Moreover, it offers no provisions for crack detection and elimination. Therefore, while the rotor blade lifetime is significantly extended, the blades still have to undergo expensive non-destructive testing techniques to detect cracks.

Introduction of the novel self-healing polymer composite between the fiberglass layers has the potential to prevent, or in the very least reduce, debonding and delamination within the rotor blade. While the inspection costs are not likely to be reduced, particularly in the short-term, because the trust in the new material has not yet been established, the repair costs can be lowered significantly over the life time of the aircraft. The material can be applied universally to any helicopter model that has fiberglass layers in its rotor blades.

There are some barriers to entry into this industry that need to be overcome prior to commercialization of the self-healing material. These barriers include stringent regulations on materials, as well as integration with the current manufacturing process and design of the rotor blade. The fiberglass skin is created via a layup process, and the self-healing composite could be introduced into the skin by impregnating the layers, either using a hard plastic applicator, or a brush, prior to curing the polymer [9].

3.5 Application Selection

After analyzing the four potential applications, it is possible to make an informed decision regarding the choice of technology to pursue in the short-term. The hip joint replacement could be ruled out based on the inability of the novel self-healing composite to provide a structural material that would be able to carry the loads required by the application, as well as the inability to compete with the cost of the materials currently utilized for hip joint replacement parts. Pursuing the automotive coating application would be undesirable as well, due to the competing emerging self-healing technology that is specifically tailored toward the coating application, is cheaper than the self-healing design at hand, and is presently market ready.

From the remaining two applications, microelectronics packaging is less favorable than the helicopter rotor blade because it presents more technological barriers that need to be overcome before the self-healing design could be successfully integrated with the current technology. Thus, of the four applications analyzed above, the optimal technology to pursue in the short-term is the helicopter rotor blade.

4. Helicopter Market Analysis

The helicopter market is divided into two major sectors: civil and military. An overview of each sector is provided below. Overall market characteristics are explored, and factors influencing the market are analyzed. Supply and demand chain is presented.

4.1 Civil Helicopter Market

Today, the civil helicopter market boom is leaving manufacturers struggling to meet customers' demands. In four years, the number of helicopters sold domestically and for export in the civil market has doubled [20]. (See Fig. 12.) The need to replace aging helicopter models and a relatively strong economic growth have been the reasons behind the civil market boom. The industry is expected to maintain high production levels in the next ten years, even if demand falls below today's record highs. (See Fig. 13.)

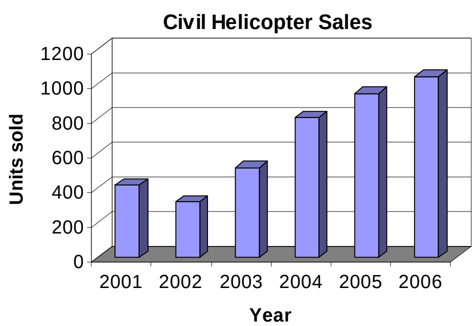

Fig. 12 Domestic and export civil helicopter sales. [20]

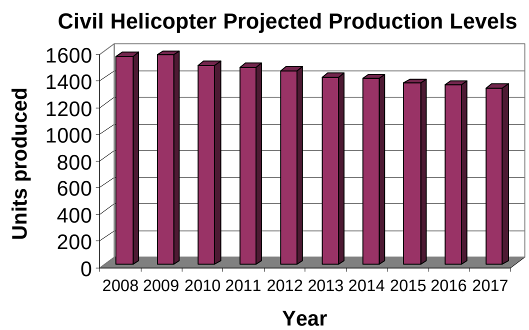

Fig. 13 Civil helicopter production levels projected over the next 10 years. [20]

Optimistic projections for future production levels of civil helicopters are based on expanding current markets, emerging new markets, and strong economic growth worldwide. Traditionally, there has been strong demand in the western markets. In addition, India and China are expected to incrementally develop into major markets, due to emerging business class and growing demand by the government. The timeline for growth in the China market is difficult to predict, as restrictions on civil flights in the country's airspace are vast and stringent. Expanding economies in Latin America and Eastern Europe promise additional opportunities for helicopter manufacturers [20].

The civil helicopter production market in the United States is highly concentrated. As indicated on Fig. 14, five manufacturers hold almost 90% of the market share (on the basis of unit production). It is expected that in the next ten years, the market will remain dominated by these five companies, although percentage of the market held by each company may change. While Robinson holds over 40% of the market in terms of number of units produced, its market share value-wise is significantly smaller. Robinson specializes in piston-powered helicopters, which hold price tags on the order of $350,000 to $450,000 per unit. The other four major players produce turbine-powered helicopters almost exclusively. Such aircraft costs on the order of $3,000,000 to $13,000,000. Robinson has been developing a new turbine-powered helicopter model, and it is expected to remain a competitive player in the civil helicopter market.

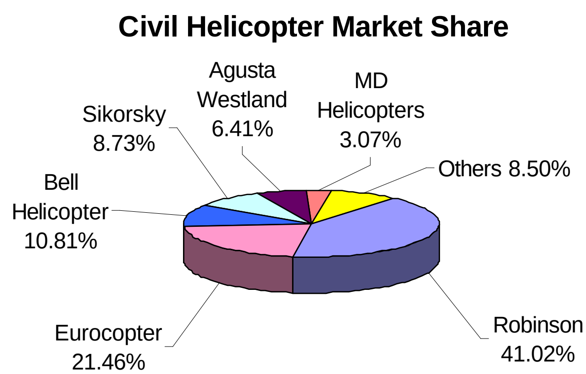

Fig. 14 Civil helicopter market share division, unit based. [20]

Improvements to current models, as well as revolutionary new designs that are presently being considered, increase the chances of new helicopter sales. Improved avionics and performance, higher mission availability rates, and lower costs of operation are some of the characteristics that customers are searching for. Reduced repair costs and lower risks of delamination damage, due to introduction of the novel self-healing polymer composite into the helicopter blades, would address some of these demands for future helicopter designs.

4.2 Military Helicopter Market

As mentioned previously, the civil helicopter market has expanded drastically in the past several years. In 2007, the civil market was valued at two billion dollars. As large as that number seems, the civil helicopter market makes up only 23% of the total rotorcraft market. The other 77% of the market are divided among various military market functions, such as scout or attack helicopters, naval (anti-submarine and anti-surface warfare) rotorcraft, and the relatively new tiltrotor models. The military market in 2007 was valued at 6.7 billion dollars. Therefore, the entire rotorcraft market in 2007 was estimated to be 8.7 billion dollars. Not only is the military market significantly larger, it is also expected to grow faster than the civil helicopter market (see Fig. 15).

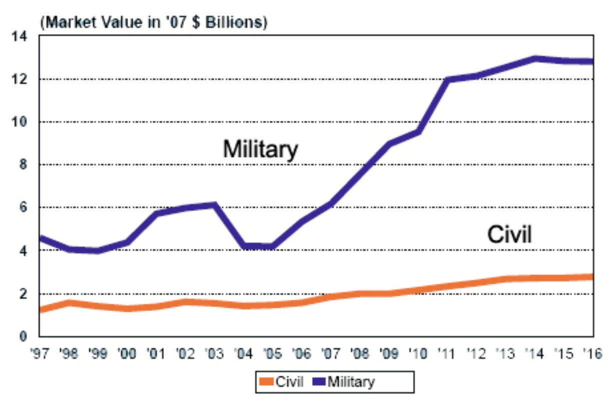

Fig. 15 Military and civil market value: past values and future projections. [20]

Like the civil helicopter market, the military market is highly concentrated. As a result, the entire rotorcraft market is dominated by five major players, which control over 90% of the market (value-based). (See Fig. 16.) Boeing is the obvious leader of the market, with over 25% of the market share. In the next ten years, the market is expected to become even more concentrated among these five players, leaving only 2.6% for all other manufacturers. Boeing is expected to capture over 30% of the market in the ten-year span.

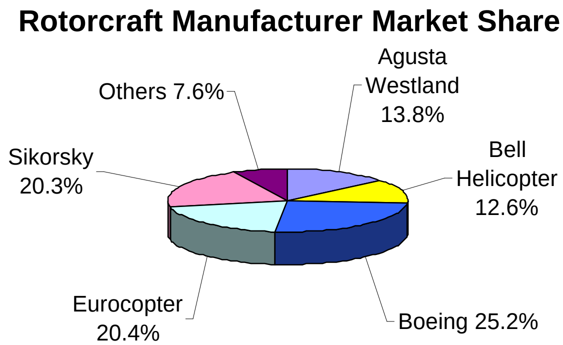

Fig. 16 Combined military and civil market share division, value based. [20]

4.3 Market Characteristics

The helicopter manufacturing industry is characterized by high barriers of entry, due to the following reasons. A new product company wishing to enter the market will encounter high start-up costs, which include the cost of land, plant, technology, equipment, and labor. Entry into the market is further hindered due to the fact that subsidies and grants are provided to incumbent players. Also, the industry is under heavy and stringent regulations, which apply to licensing of manufacturers and security clearance issues. For these reasons, the industry experiences a low annual growth (less than one percent) of the number of new establishments. Another reason for stagnating new establishment numbers in the domestic market is outsourcing by major players of their manufacturing base to low cost producing countries, such as China and India. In the military/defense sector, many participants rely on government contracts for survival. Another characteristic of the industry is the requirement of highly skilled labor, as well as a constant need for adaptation to new technology. These high barriers of entry favor the growth of existing companies, while limiting new entrants into the industry [21].

In the military/defense sector, investment in research and development, as well as state of the art technology in aerospace products, allows companies to gain competitive advantage. A constant stream of innovation is a characteristic of the defense industry. This sector utilizes more advanced equipment and materials than the civil segment, which is a desirable market characteristic for introduction of novel materials. However, there is an additional barrier to entry into the defense sector. Contracts tend to go to the companies with brand recognition and previous exposure to military applications [21]. Usually, the major players bid for the government contracts, and then subcontract specific systems and parts to smaller firms. Therefore, entry into the market might be easier at the level of parts manufacturing. However, as a trade-off, smaller firms with subcontracts are subject to the requirements of the major players, which can potentially translate to lower margins and profits. The majority of revenue is earned by the main contractors.

4.4 Market Demand Influence Factors

There are several factors that influence the demand for aircraft products in general, and rotorcraft products specifically. An obvious factor is the price of the product. The more affordable the rotorcraft models enjoy a larger potential pool of buyers. Market statistics clearly indicate the strong influence of the price factor – in 2006, Robinson's significantly cheaper piston-powered helicopters amounted for more than half of the total annual civil helicopter sales in the United States [20].

A related factor that affects demand is household disposable income. Historically, a larger available disposable income leads to bigger spending. Disposable income itself is influenced by domestic interest and tax rates, employment levels, and household savings rate. In other words, a strong and growing economy generally translates to higher household disposable income, which positive affects the demand for aircraft products.

Another important market demand influence factor is the global price of oil. An increased price of aviation fuel would make aircraft operations more costly, and would dampen the demand for new aircraft. Also, the resale levels (or alternatively, resale prices) of older, less fuel efficient models would decrease. However, one positive aspect of high oil prices is a growing demand for new, more fuel-efficient designs, particularly in markets that can not afford to reduce levels of aircraft operation, such as the large military sector of the helicopter market.

The level of defense spending is a significant factor in determining the level of demand for aircraft. An ongoing war, or preparation for an increased level in national defense, as well as events such as terrorist attacks would result in a higher level of defense spending. Because over two thirds of the rotorcraft market is determined by the military sector, increased defense spending would directly increase the demand for military helicopters. One important drawback of defense spending is low profit margins associated with the government contracts.

A less direct market demand factor is technological innovation. This factor does not correlate as directly and obviously with market demand as the factors listed previously due to the nature of emergence of new technology on the market. Often, the military sector drives technological innovation. Therefore, other factors, such as increased need for better national defense, higher level of defense spending, and the stability and growth of the economy influence the amount of resources the government is willing to spend on technological advances. More directly, the level of technological innovation depends on the funds the government allocates to research and development. Once innovation programs are set in motion, and new technologies appear on the military market, the demand for the new and improved designs in the civil market is likely to result.

Globalization is another factor that tends to increase the demand for aircraft, as companies and businesses expand beyond their origination regions. Evidence of globalization effect is clear in the civil helicopter market – exports in this sector increased by 57% in 2007, as compared to the previous year, and amounted to a record $490 million [21].

4.5 Competition within Market

In order to become and remain competitive within the aircraft market, a company needs to be aware of the following factors. Within the civil sector, price and product innovation are taken into consideration by potential customers during the process of selection of the desired aircraft model. Some of the most important innovation categories include fuel efficiency, operating costs, and maintenance/repair costs. The total package price, which includes post-sale support and life cycle logistics operations, is a significant factor in a purchase decision. Another competition factor within the civil market is brand and consumer preference for various types of aircraft.

Within the military market, price is also a major competitive factor. Defense contracts are negotiated and awarded via a complicated process, with price being one of the primary considerations. Competitive advantage could be achieved by investing in research and development in order to constantly introduce innovation into the company's products. Within the military sector, established brand recognition is an important factor to the Department of Defense, and other government organizations.

4.6 Supply and Demand Chain

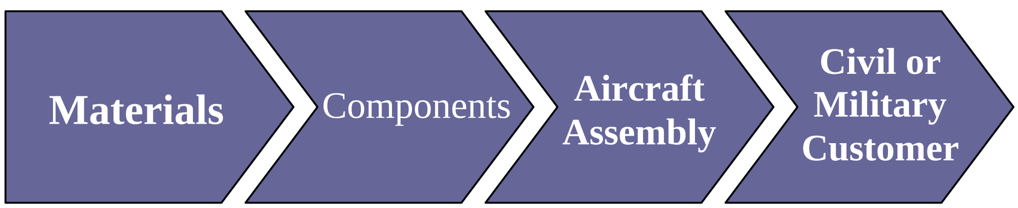

Fig. 17 Supply and Demand chain for the helicopter manufacturing market.

The supply chain for the helicopter manufacturing market starts at the level of materials. Materials include metals, such as steel and titanium, various plastics, and composites, such as fiberglass in epoxy matrix. Materials are shipped to subcontractors that manufacture various components of the helicopter. These components include the airframe, blades, engine, electronics, and interior cabin parts. In some cases, some of these components are produced directly by the Original Equipment Manufacturers

(OEMs). OEMs are responsible for the third level of the supply and demand chain – rotorcraft assembly. Manufacturers then sell the final product, the helicopter, to the customer, which can be part of either the civil or the military sector of the market.

The demand chain is better illustrated by analyzing the supply and demand chain from the customer level. Unlike some of the other types of transportation, such as automobiles, helicopters are not mass-produced. Most models are designed to satisfy a customer's specifications, whether the customer is an individual, a private business, or the federal government. Therefore, the demand for different types of components can vary greatly from year to year. However, the industry utilizes a more or less established set of materials. Thus, while the amount of materials necessary per fiscal year is not trivial to predict, the types of materials needed in the industry are well known.

The novel autonomous self-healing polymer composite would be introduced at the level of materials, and would be incorporated into the manufacturing process of components manufacturers. While entering the market at the lowest level of the supply chain means lower barriers of entry due to high competition among larger number of establishments, rather than attempting to establish an aircraft manufacturing company in a highly concentrated market, there is a major drawback to such strategy. The new company introducing this novel material into the helicopter manufacturing industry would face the regulations and established relationships of the entire supply and demand chain, and therefore would likely experience low profit margins.

5. Cost Analysis and Market Entry

5.1 Material Production Cost Estimate

The following is an estimate of production cost of both designs of the novel autonomous self-healing polymer composite. The cost analysis is based on the prices of raw materials. Therefore, in order to account for production process costs, production cost values utilized in further calculations are higher than the materials-based values.

5.1.1 Design #1: Microencapsulation

Table 2. Design #1 cost estimation.

Material	Conc.	Cost	Cost/100 g	% Total Cost
EPON 828	92.5%	$2.5/kg	$0.23	0.12%
Microcapsule	5.0%	* $4.51/g	$22.57	12.13%
Grubbs catalyst	2.5%	$65.3/g	$163.25	87.75%
			$186.05	

Note: Concentration values are in weight %.

*Microcapsule estimated cost:
7 g urea at $19.40/100 g: $1.36
0.23 mL 37% formaldehyde at $22.80/500 mL: $0.01
60 mL DCPD at $26/500 g with 0.986 g/mL density: $3.08

Total: $4.45 per 60 mL DCPD, but with 80% yield:
$4.45 per 48 mL DCPD
At 1 mL/0.986 g specific volume: $4.51/g

Price Sources
EPON 828: Cambridge Educational Software (CES)
Grubbs catalyst: Sigma Aldrich
DCPD: Sigma Aldrich
Urea: Sigma Aldrich
Formaldehyde: Sigma Aldrich

Volume of 100g estimate:
Since epoxy makes up the bulk of the volume, base volume calculations on epoxy density.
92.5 g / 1.16 g/cm^3 = 79.7cm^3

Design #1 Cost	
~ $200 / 100 g	(conservative estimate)
~ $5 / cm^2	(based on 20 mm thickness)

5.1.2 Design #2: Microvascular Network

Table 3. Design #2 cost estimation.

Material	Conc.	Cost	Cost/100 g	% Total Cost
EPON 828	85.0%	$2.5/kg	$0.22	0.03%
DCPD	5.0%	$4.51/g	$22.57	3.34%
Grubbs catalyst	10.0%	$65.3/g	$653.00	96.63%
			$675.79	

Note: Concentration values are in weight %.

Volume of 100g estimate:
Since epoxy makes up the bulk of the volume, base volume calculations on epoxy density.
85 g / 1.16 g/cm^3 = 73.27cm^3

Assumption: total volume of DCPD in microchannels is eqivalent to total volume of DCPD in microcapsules in Design #1

Design #2 Cost	
~ $700 / 100 g	(conservative estimate)
~ $6.70 / cm^2	(based on 7 mm thickness)

As is evident from Tables 2 and 3, the Grubbs catalyst is responsible for the majority of the cost of the novel material – over 87% in the microencapsulation design and 96% in the microvascular network design. The cost of both designs could be significantly reduced if the Grubbs catalyst is successfully replaced by the much more affordable organic solvents – for instance, the price of chlorobenzene is only $0.09 per gram (based on Fisher Scientific price).

5.2 Cost per Helicopter Blade

To understand the marketability of the novel design, the cost of material in a specific application needs to be estimated. For the purpose of this analysis, the popular Robinson R22 helicopter model is presented as the application of interest. The R22 model is a two blade helicopter, with the following blade dimensions:

Length	383.54 cm
Width	18.29 cm
Area	7,014 cm^2

The cost of incorporating one layer of the microencapsulation design version of the self-healing material into one blade, assuming the layer spans the entirety of the blade, is $35,070. Considering that a replacement R22 blade costs $13,000 [18], the current self-healing design is completely unmarketable.

Before the novel self-healing material can become competitive in the current market, it has to be drastically modified. More specifically, the most expensive component of the polymer composite needs to be replaced by a much more affordable material. Based on the ongoing research [8], it seems feasible to successfully remove the extremely expensive Grubbs catalyst from the formulation and replace it with an organic solvent based system. A self-healing design based on epoxy matrix with a dispersion of chlorobenzene-filled poly-urea microcapsules has been shown to provide the desired autonomous self-healing characteristics. The following cost analysis of this design assumes 1 mm thickness of the material, which is within realistic parameters, as encapsulation on an even smaller nanoscale has been successfully demonstrated [12].

Table 4. Solvent-based design cost estimation.

Material	Conc.	Cost/100 g
EPON 828	80%	$0.20
Chlorobenzene microcapsule	20%	$2.77
		$2.97

Note: Concentration values are in weight %.

*Chlorobenzene Microcapsule estimated cost:
7 g urea at $19.40/100 g: $1.36
0.23 mL 37% formaldehyde at $22.80/500 mL: $0.01
60 mL chlorobenzene at $0.09 per gram (1.106 g/mL density): $5.97

Total: $7.34 per 60 mL chlorobenzene, but assuming 80% yield:
$7.34 per 48 mL chlorobenzene
At 1 mL/1.106 g specific volume: $0.1383/g

Volume of 100g estimate:
Epoxy fraction: 80g / 1.16 g/cm^3 = 68.96 cm^3
Chlorobenzene fraction: 20g / 1.106 g/cm^3 = 18.09 cm^3
Total volume: 87.05 cm^3

Solvent-based Design Cost	
~ $4 / 100 g	(conservative estimate)
~ $0.046 / cm^2	(based on 1 mm thickness)

The cost of incorporating one layer of the solvent-based design version of the self-healing material into one R22 blade, assuming the layer spans the entirety of the blade, is $323, based on conservative material cost estimates.

5.3 Competing Product

Airwolf Aerospace has developed a polymer tape that is designed to seal helicopter blades in order to protect them from moisture that causes delamination [18]. The polymer tape is applied externally to the surface of the blade. Currently, Federal Aviation

Administration (FAA) has approved polymer tape kits that are available for two helicopter models: Robinson R22 and R44. The cost per kit is $1,200 for the R22 blades, and $2,500 for the R44 model. The application of the polymer tape is not incorporated into the blade manufacturing process; instead, the tape is applied onto already fully manufactured helicopters. Because FAA requires the blades to be removed prior to applying the polymer tape, labor costs need to be taken into account in addition to the price of the tape kits [22]. FAA estimates the removal and replacement of the blades to last ten working hours, at an average labor rate of $80 per hour. Therefore, additional $800 in labor costs are incurred during the tape application process, bringing the total price of the Airwolf polymer tape kits to $2,000 and $3,300.

Airwolf Aerospace product offers delamination solution only for the outer layer of the blade’s skin. It offers no provisions for reducing the chance of delamination between the internal fiberglass skin layers. It also does not resolve the issue of internal and external microcrack formation. Currently, the product is limited to two helicopter models, leaving the rest of the helicopter market without a delamination solution. The current method of dealing with formation of external microcracks, which could potentially lead to delamination, is repainting the blade upon discovery of the cracks. However, this method does not prevent the formation of cracks, and is not effective in propagation prevention of the undiscovered microcracks.

While Airwolf Aerospace has developed the polymer tape kit for only two helicopter models, they have nevertheless managed to capture a significant share of the market –

Robinson produces more than 40% of the civil helicopters (see Fig. 14). However, Robinson helicopters are some of the cheapest in the civil market, and the combined helicopter market is lead by the military segment. Therefore, value-wise, Robinson is not a major player in the helicopter market (see Fig. 16). Thus, over 90% of the total helicopter market, including the significantly more expensive military models, does not yet have an efficient way of dealing with microcracks and delamination in the blades. It is likely, however, that Airwolf Aerospace will attempt to pursue FAA approval for applying their polymer tape to other helicopter models.

At this stage of the novel polymer development, it is difficult to predict the costs associated with incorporating the new material into the current blade manufacturing process. Therefore, the following comparison of the novel material with the Airwolf polymer tape does not include the labor costs incurred with applying the Airwolf product. For the R22 model, the polymer tape kit costs $1,200. Assuming the kit contains enough tape to cover both blades, the cost is $600 per blade. Approximately two layers of the novel self-healing polymer composite could be incorporated into the blade for the same price. For the R44 model, the tape kit costs $2,500, which translates to $1,250 per blade. Approximately three layers of the novel self-healing polymer could be incorporated into the blade for that price. In other words, the novel material becomes more competitive on a larger scale, in terms of both blade geometry and the production level.

The novel autonomous self-healing polymer composite offers a solution for prevention of microcrack propagation and delamination on the interior and exterior of the helicopter blade. Internally, it can be applied in any type of helicopter blade that contains fiberglass skin layers.

5.4 Market Entry Timeline

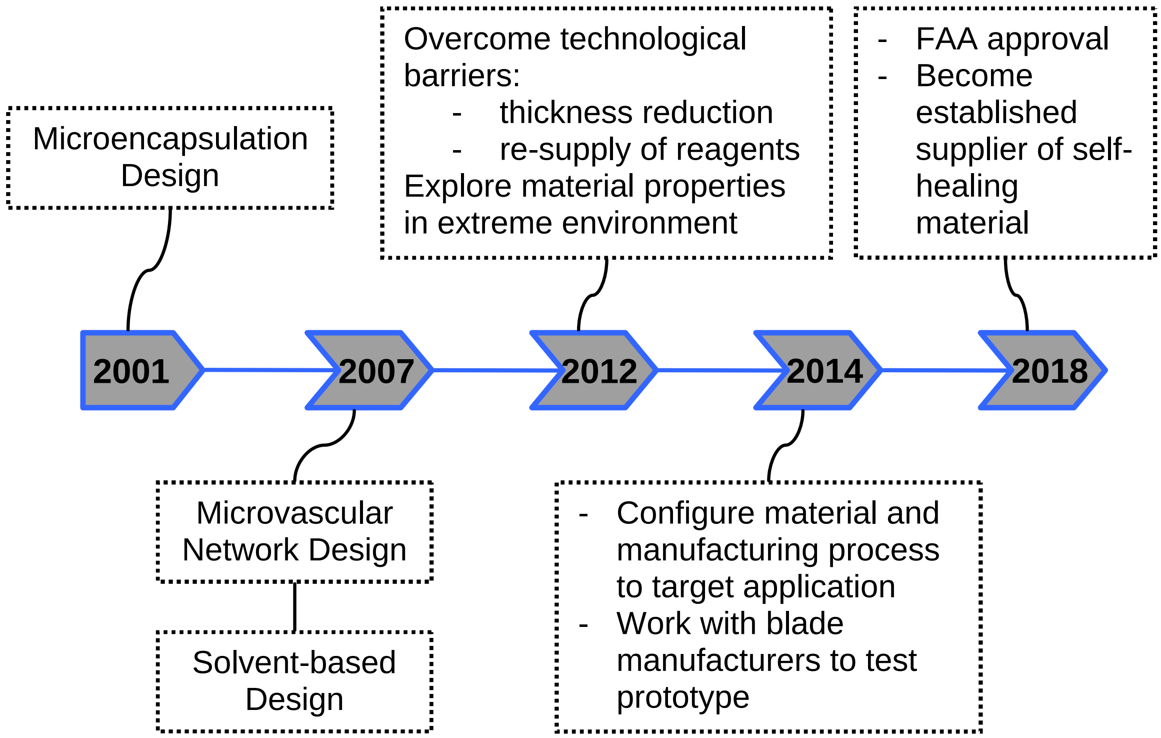

Fig. 18 Market entry timeline.

Part of the research segment of the market entry timeline has already been completed. In 2001, the microencapsulation design of the autonomous self-healing material was invented. Six years later, further research lead to the microvascular network design and the solvent-promoted self-healing design.

Because this novel technology is still in its research stage of the development, it is not yet market ready. In order to be able to enter the market, several technological barriers have to be overcome. For instance, the two current designs are too thick to be incorporated into the skin of the helicopter blade. Thus, the thickness of the material needs to be reduced. While encapsulation of the healing reagents on the nanoscale has been successfully demonstrated [12], the self-healing ability of nanocapsules is yet to be proven. Another major technological issue that needs to be resolved is the re-supply of the self-healing reagents into the bulk of the material. Behavior and properties of the novel material in extreme and damaging environment needs to be explored. The technological issues listed above are expected to be resolved by the year 2012.

Once the design of the self-healing material is finalized, it needs to be incorporated into the process of helicopter blade manufacturing. In order to accomplish this, the material designers need to work closely with the helicopter blade manufacturers to test the material prototype. The customized material is expected to be fully and successfully integrated into the blade manufacturing process by the year 2014.

After sufficient amount of testing of the material embedded into the target application, FAA approval needs to be obtained. This approval is necessary to be able to sell the novel material to rotorcraft parts manufacturers. Because FAA approval process is a long one, this segment of the market entry timeline is expected to last approximately four years. By 2018, the company expects to become an established supplier of the novel autonomous self-healing material to the helicopter blade manufacturers, if it decides to pursue the product manufacturing business strategy.

6. Intellectual Property Landscape

6.1 Owned Intellectual Property

Presently, the original inventors of the novel autonomous self-healing polymer composite hold two patents in the United States. Patent **6,518,330** [23] ("Multifunctional autonomically healing composite material") provides broad intellectual property coverage for the microencapsulation design. This patent was filed on February 13, 2001. The patent describes a self-healing composite material that consists of a polymer, a polymerizer, and a corresponding catalyst for the polymerizer. The polymerizer is contained within a multitude of capsules. The patent claims that the polymerizer in this composite material is at least one monomer selected from the following groups: cyclic olefins, lactones, lactams, acrylates, acrylic acids, alkyl acrylades, alkyl acrylic acids, styrenes, isoprene, and butadiene. The polymer is at least one member from the following groups: polyamides, polyesters, polycarbonates, polyethers, polyimides, phenol-formaldehyde resins, amine formaldehyde resins, polysulfones, poly (acrylonitrile-butadiene-styrene), polyurethanes, polyolefins, and polysilanes. The catalyst corresponding to the polymerizer can be either a ROMP catalyst or a cyclic ester polymerization catalyst. The capsules containing the polymerizer have an aspect ratio of 1:1 to 1:2, and an average diameter of 10 nm to 1 mm. Capsules can be made of urea and formaldehyde, gelatin, polyurea, and polyamide. One of the claims specifies the configuration of the microencapsulation design as described in the "Designs of Self-

Healing Materials" chapter. The patent also claims the method for making the self-healing composite, namely dispersing the capsules and the corresponding catalyst into the polymer.

The second patent is the continuation of the first, and holds the same title. Patent **6,858,659** [24] was filed on October 25, 2002. This patent extends the claims to a self-healing polymer composite with the following configuration. The composite consists of a polymer, a polymerizer, and a corresponding activator. The polymerizer is contained in capsules, and is defined as a monomer and a first part of a two-part catalyst. The activator is the second part of the same catalyst, and it could be contained within a second type of capsules. The patent also claims the method for making such composite. The inventors also hold an international patent covering these claims, titled "Self-healing polymers" (**WO/2006/121609**) [25] which was filed on April 26, 2006.

The inventors also hold an international patent titled "Self-healing coating system" (**WO/2007/82153**) [26], which was filed on January 5, 2007. The patent claims a composition of polymer matrix, polymerizer, and a corresponding encapsulated activator for the polymerizer. The polymerizer could be either in capsules or phase separated from the matrix. Specifically, the patent claims capsules filled with a siloxane polymerizer, and another set of capsules with the corresponding activator. The activator is a catalyst that could be selected from a group of amines and salt metals. Same aspect ratios and average diameters for the capsules are claimed as in the patents listed above. An additional claim states that the composition could additionally contain a matrix precursor. The patent also claims the method for creating such composition by combining the individual components. Another claim covers the method of making the coating by contacting the composition with a substrate, and allowing the composition to solidify. In addition, the polymerizer and the activator in the composition could be wet-curable. Subsequently, another claim covers the method of protecting a coated surface by placing it in contact with water in order to cure the polymerizer. Lastly, kits containing these various compositions are claimed.

The original inventors have filed five additional U.S. patent applications. The first patent application titled “Self-healing elastomer system” (**11/421,993**) [27] was filed on June 2, 2006, and it claims a microencapsulation design of a composite material with an elastomer matrix, such as a polysiloxane. Matrix polymer groups include elastomer polymers, copolymer elastomers, block copolymer elastomers, and polymer blend elastomers. In addition to a polymer, encapsulated polymerizer, and encapsulated activator, the composite could include an adhesion promoter. The activator, or catalyst, could be from a group of amines or metal salts. The method for making such composite is also claimed. The inventors hold an international patent on the self-healing elastomer system (**WO/2007/143475**) [28], filed on May 30, 2007.

Another patent application filed by the original inventors on May 31, 2007 covers in detail the method of encapsulation. It is titled “Capsules, methods for making capsules, and self-healing composites including the same” (**11/756,280**) [29]. Patent application titled “Self-healing materials with microfluidic networks” (**11/760,567**) [30] filed on June

8, 2007 covers the microvascular network self-healing design. The solvent-based self-healing design patent application was filed on October 26, 2007 under the title "Solvent-promoted self healing materials" (**60/983,004**) [31]. The latest patent application filed by the inventors covers the carbon-reinforced self-healing composite. It is titled "Self healing laminate system" (**61/023,698**) [32] and it was filed on January 25, 2008.

6.2 Competing Intellectual Property

In the recent years, competing patents have begun to populate the intellectual property landscape. On March 4, 2003, a patent titled "Self-healing coating and microcapsules to make same" (**7,192,993**) [33] was filed by the Secretary of the Army. The patent claims a self-healing coating, which is cured at an ambient temperature, and consists of the following components: at least one liquid commercial off-the-shelf (COTS) coating; spherical microcapsules suitable for wet mixing with the liquid COTS coating, with an approximate diameter of 150 μm; at least one repair substance contained within the microcapsules. The microcapsule shell has to be resistant to degradation by the repair substance and the liquid COTS coating. The claims include a method of mixing the microcapsules into the COTS coating just prior to the application of the self-healing coating. In case of a physical compromise of the cured coating, the capsules burst and the repair substance fills and seals the compromised volume within the coating. While this patent aims at the same coating application as the "Self-healing coating system" (**WO/2007/82153**) [26] patent, it does not infringe upon the novel autonomous self-healing polymer composite because it does not contain a polymer based matrix.

On July 15, 2002, a patent titled “Self-healing polymer compositions” (**7,108,914**) [34] was filed by Motorola. The patent claims a self-healing polymer composition consisting of the following components: a polymer media and microcapsules filled with flowable polymerizable material, where at least one type of polymerization agent is chemically attached to the outer surface of at least some of the microcapsules via a molecular bridging unit. Upon failure of the polymer media, the microcapsules rupture, the polymerizable material is released and it reacts with the polymerization agent. Additionally, a solvent can be included inside the microcapsules in order to facilitate the flow of the polymerizable material. The microcapsules could have a metal film on the outer surface to promote chemical attachment of the polymerization agent. The microcapsule shell could be made of a hydrous metal oxide, silica, silicate, carbon, polymer, or mixtures of any of these compounds. There could be a matrix layer of thiol moieties, which would be chemically attached to the metal film via a molecular bridging unit. The bridging unit would have a carbon-carbon backbone, and a norbornenyl or a norbornenyl derivative group on one end. The outer surface of the microcapsules could be covered with a bonding silanization agent. The polymerization agent could be selected from a group of derivatives of aluminum, titanium, or tin, as well as a group of ruthenium complex, osmium complex, and indium complex. The polymerizable material could be norbornene, alkyl substituted norbornene derivatives, alkoxysilynorbornenes, DCPD, DCPD oligamers, or DCPD copolymers. The polymer media could be chosen from thermoset, thermoplastic, or elastomeric materials. While this self-healing composition strongly resembles the microencapsulation design, it is nevertheless sufficiently different in its requirement to chemically attach the polymerization agent to the surface of the microcapsules containing the polymerizable material. Therefore, this patent does not infringe on the patents of the original inventors. However, it aims to address the same microcrack formation issues as the novel autonomous self-healing material, and is therefore a competing patent.

On October 16, 2003, a patent titled “Method for self-healing cracks in underfill material between an I/C chip and a substrate bonded together with solder balls” (**7,045,562**) [35] was filed by IBM. The patent claims a composition for self-healing of cracks formed in the underfill material between the I/C chip and the circuitized substrate. The composition consists of the following components: the underfill materials has a cured epoxy base with a dispersion of capsules; the capsules have a rupturable shell filled with curable thermosetting adhesive; a curing agent that causes a reaction of the thermosetting adhesive upon contact in order to form a cured adhesive inside the crack. The curing agent is a ruthenium based catalyst. The capsules are less than 25 μm in diameter, with a urea formaldehyde shell. The thermosetting adhesive is DCPD. There are 5% to 20% by weight of capsules in the underfill material, as well as up to 5% by weight of the curing agent. This patent directly competes with the microencapsulation design, as it applies the design to a specific application, namely the underfill material in the integrated circuit chip.

On October 8, 2003, a patent titled “Process of self-repair of insulation material” (**7,285,306**) [36] was filed by NASA. The patent claims a self-repair process specific to repairing insulation material on a wire conductor. Microcapsules with reactants can be either applied to the outer side of the insulation material or be dispersed within it. There are two reactants in the microcapsules, which react upon rupture of the capsule in order to form a replacement polymer that repairs the insulation material. The two reactants can be selected from a group of: monomers, catalysts, reactants that form condensation polymer, fusible polymers, and chemical heaters. For example, the first reactant could be a dianhydrite while the second reactant is a diamine, or the first reactant could be a fusible polymer, such as polyfluorocarbon, and the second reactant would be a chemical heater. Both reactants could be within the same microcapsule, separated by a polymer shell. The microcapsule size is 5 to 500 μm in diameter. The insulation material could contain a polyimide, in which case the replacement polymer would also be a polyimide. Besides the configuration where the two reactants are within the same microcapsule, this patent directly competes with the microencapsulation design for the specific application of insulation material for conducting wires.

6.3 Developing IP Strategy

The original inventors have taken several necessary steps to protect their various novel self-healing designs, such as the microencapsulation design, the microvascular network design, the solvent-based design, the elastomer based system, and the carbon-reinforced self-healing composite. However, the existing intellectual property, in form of patents and patent applications, does not cover any specific applications of any of these designs, except for one international patent on a self-healing coating system. This is a dangerous situation for a company that is attempting to commercialize the novel technology, particularly because the existing competing patents are targeting specific applications for the microencapsulation self-healing design.

An important and essential strategy for developing and expanding the intellectual property landscape of the original inventors needs to include patents that cover specific short-term and long-term applications that will be utilizing the self-healing designs. The growth of the intellectual property landscape needs to include applications of all of the various self-healing designs to specific technologies. Particularly, the IP coverage for the solvent-promoted self-healing design needs to be improved, as this seems to be the most cost efficient design to date that is likely to succeed in the commercialization process.

Another point of concern in the commercialization process is expiration of patents. Based on the estimated timeline (see Fig. 18), the company is expected to become fully operational in the year 2018. Since patents expire twenty years after their original filing date, the first patents filed by the original inventors will begin to expire in the year 2021, leaving only three years of protected intellectual property for the existing company, provided its establishment follows the predicted timeline. Therefore, it is necessary for the company to continue evolving its intellectual landscape all throughout the development and commercialization process.

7. Business Strategy

In order to successfully enter the market, the company needs to select an appropriate business strategy. While many business models are available to start-up companies, two that make sense for introducing the novel autonomous self-healing composite to the helicopter market are the intellectual property licensing and the product manufacturing strategies.

7.1 IP Licensing

Licensing out the intellectual property on the novel self-healing material to an existing helicopter blade manufacturing company could potentially be advantageous. It would allow the licensor company to focus on further research and product development, while collecting royalties from the licensee company, which has the expertise and the production volume to more efficiently manufacture products using the novel material. This could also help speed up the entry into the market, ahead of any potential competitors. In order to reap the most benefits from the IP transfer, the licensor needs to make sure that the license agreement clearly defines the rights being transferred, such as selling products that incorporate the novel technology in a specific manner, for a specific time period in a specified region [37]. In short, a license agreement would allow the licensor to retain the ownership of the intellectual property, while receiving royalties in addition to the income from its own exploitations of the IP in products and services that it sells, should the licensor decide to manufacture any products in-house.

While intellectual property licensing might seem like the appropriate business model for the start-up company, this strategy involves some potentially serious risks. One obvious risk is that the company’s own investment in the manufacturing process could turn out to be more profitable than the license agreement. Another potential risk is that the licensee could become a competitor in the long run by acquiring the know-how from the licensor while expanding its IP portfolio and waiting for the original patents to expire. The licensor also runs the risk of receiving little or no royalty revenue if the licensee proves to be ineffective in manufacturing and getting the product to market in a quick and efficient manner. When transferring property rights, the licensor becomes dependent on the skills, abilities, and resources of the licensee to provide revenue in the form of royalty fees. Also, if the product or technology is not clearly defined or complete at the time of the license agreement establishment, the licensor is likely to incur heavy investment costs in the expensive development work in order to satisfy the licensee. This is an important risk to take into consideration for the novel material inventors, as the technology is currently not in a well-defined or completed stage.

In order for the license agreement to be established, the licensee also needs to consider the costs and the benefits involved in the intellectual property rights transfer. By signing a license agreement, the licensee could gain a competitive advantage in the market by incorporating the novel superior technology into its products ahead of its competitors. However, the licensee runs the risk of making a financial commitment to a technology that might not be ready for commercialization. The licensee also needs to take into consideration the additional layer of expense that the IP license applies to the product. The market has to be able to sustain the new elevated price of the improved technology.

7.2 Product Manufacturing

The obvious advantage of choosing a product manufacturing business strategy for the start-up company is that the revenue generated from the sales of the product goes directly to the company. The company is aware of the skills, abilities and resources available to efficiently launch the new product into the market. However, there are numerous risks associated with starting a product company.

Before a product becomes ready to enter the market, the company invests a lot of time and money into its research and development, all the while running the risk of not being able to commercialize it at the end of the process. This could be due to R&D issues, such as running into a technological barrier that could not be overcome, or realizing that incorporating the novel material into the target application requires a major change in the manufacturing process of the application, which is not likely to be implemented within an established industry. The product might also not be commercialized due to market-side problems. The additional expense caused by the incorporation of the new material might cause the price of the application to rise above the market sustainability price. It is also possible that despite the optimistic market growth projections, unexpected factors could arise that would negatively influence the demand for the application.

The company has to be able to launch the product into the market before its competitors do. Therefore, the timeline needs to account for patent expiration dates and time to obtain FAA approval for the novel material – something that the company would not have to worry about if it licenses out its intellectual property to a manufacturer. During the development timeline, the company has to establish relationships with important players on all levels of the supply chain, and convince them of the value that will be added to each level of the chain by the new product. Another concern for a start-up company entering the market at the lowest (materials) level of the supply chain is potentially low profit margins and regulations established by companies higher up on the chain.

7.3 Strategy of Choice

If the company chooses to pursue the product manufacturing business model, assuming everything goes well and the product is successfully launched, the company is still very likely to face low profit margins. In order to pursue the intellectual property licensing business model, the company has to complete the development of the novel material and overcome all the remaining technological barriers. It would also most likely need to provide a functional application prototype to the potential licensee, which would require a significant amount of investment in research and development.

In order to avoid the likely low profit margins associated with starting a materials company, the ideal business strategy for the company introducing the novel autonomous self-healing material to the market would be to become a research and development company. A company focused on R&D would have the advantage of being able to develop new products on a low volume scale, while licensing out intellectual property from its expanding IP portfolio to manufacturing companies, thus collecting royalties on its technology without needing to obtain an FAA approval or having to invest in manufacturing facilities.

Once the initial investment amount necessary to start the business is estimated, the company needs to secure sources of funding. Some potential sources of funding include the Small Business Innovation Research (SBIR) program and the U.S. Small Business Administration (SBA). The SBIR program offers up to $850,000 in federal grants for early stage R&D funding ($100,000 in Phase I and $750,000 in Phase II), while the SBA offers loans through SBA's partners. It is not advisable to seek venture capital (VC) funding in the initial stages of the company establishment, as such funding usually involves relinquishing a significant (20-40%) portion of the company's profits to the VC firm, on top of repaying the investment loan with a high interest rate. If possible, it is desirable to receive funding from angel investors.

The combination R&D and IP licensing business strategy allows value to be added across the entire supply chain (Fig. 17). In case of the helicopter blade application, the company introduces the novel technology at the materials level. The subcontractors manufacturing the blades have access to the intellectual property for the novel technology, which they can incorporate into their product, making it competitive on the market and improving its quality, while reaping profits from the justified increase in the price of the helicopter blade. The original equipment manufacturers can offer their customers an improved product, the helicopter, with a lower risk of failure and a higher safety rating. The customers receive a better quality product that requires significantly less investment of money and time into its maintenance.

8. Conclusion

Recent breakthrough in self-healing design developed at the University of Illinois at Urbana-Champagne has enabled the development of materials capable of damage management. The self-healing designs include a mobile phase that allows the material to repair microcrack damage autonomously. While the microencapsulation design has undergone the most development, it is the solvent-based design that shows the most promise of successful commercialization.

A broad range of potential applications would benefit from the self-healing capability. Applications in the microelectronics, automotive, medical, and aerospace industries are explored, and the helicopter blade is chosen as the most likely application to succeed in introducing the novel material into the market. The novel self-healing material would decrease the failure rate of the helicopter blades due to delamination and crack formation, thus extending the lifetime of the blade. The rapidly growing helicopter market indicates continuous demand for innovation and improvement. Future forecasts predict steady growth in the helicopter market demand over the next ten years, driven by the military sector.

The autonomous self-healing material is still in the research and development phase. Numerous technological barriers have yet to be overcome before the material is ready for integration into the target application. When the technology reaches the stage of commercialization, it is recommended that the company pursues a combination business strategy of research and development and intellectual property licensing.

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Appendix: Grubbs Catalyst

Grubbs catalyst is also known as benzylidene-bis(tricyclohexylphosphine) dichlororuthenium. This catalyst is used to initiate ring-opening metathesis polymerization (ROMP) of DCPD monomer in the self-healing mechanism of the novel material discussed in the "Designs of Self-Healing Materials" chapter. The result is a room-temperature cross-linked poly(DCPD), as indicated in Fig. A1.

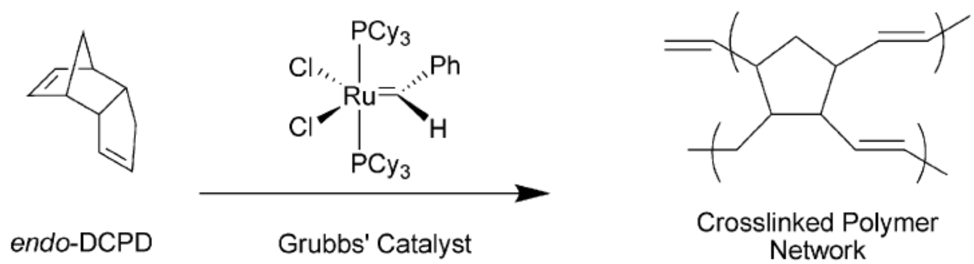

Fig. A1 Grubbs catalyst assisted ROMP of DCPD. [1]

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